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研究报告

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SO_2对MnO_x/PG催化剂低温脱硝的影响机理研究

The mechanism of SO_2 influence on the denitration of MnO_x/PG catalysts at low temperature

关键词：MnO_x/PG催化剂 硫酸铵盐 $MnSO_4$ 热处理

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摘要：采用等体积浸渍法制备了锰氧化物负载凹凸棒石(MnO_x/PG)低温SCR催化剂,通过SO_2暂态响应、程序升温表面反应(TPSR)等实验技术研究了烟气中SO_2对催化剂SCR脱硝活性的影响行为.采用程序升温脱附(TPD)、BET比表面及孔径分布测定、XPS等表征技术对催化剂硫中毒的机理及化学本质进行了深入分析.结果表明,低温下烟气中SO_2对MnO_x/PG催化剂的SCR脱硝活性存在显著的抑制作用,催化剂中毒主要由烟气中SO_2的催化氧化引起.一方面SO_2氧化为SO_3后与NH_3及H_2O竞争反应形成复杂的硫酸铵盐堵塞催化剂孔道,另一方面与活性组分MnO_2结合形成$MnSO_4$使得部分活性组分形态发生变迁.其中硫酸铵盐的形成可通过适当的热处理得以去除,而$MnSO_4$则不可恢复,但催化剂SCR活性却显著增加,表明$MnSO_4$的形成不是催化剂失活的主要因素.吸附态的硫可显著增加催化剂表面酸性,因此对SCR活性有促进作用.催化剂失活主要机理为:由气相SO_2的连续氧化并与NH_3相结合形成硫酸铵盐,并且在低温下难以分解,以致堵塞催化剂活性中心.

Abstract: MnO_x/PG, as low temperature SCR catalysts, were prepared by means of pore volume impregnation. Influences of SO_2 on the MnO_x catalysts at low temperature were investigated by transient response of SO_2 and temperature programmed surface reaction (TPSR). Catalysts were characterized by TPD, BET surface area and XPS, and the mechanism of SO_2 deactivation was discussed. The results indicated that SO_2 in the flue gas obviously inhibited the catalyst's activities for SCR at low temperature. Catalytic oxidation of SO_2 to SO_3 was mainly responsible for the poisoning of the MnO_x/PG catalysts. On one hand, SO_2 was oxidized to SO_3 and then reacted with NH_3 and H_2O to form complicated ammonium sulfates, which were then deposited on the surface of catalysts and blocked the pore; On the other hand, $MnSO_4$ was formed due to the combination of SO_3 and MnO_2, which partly changed the morphology of active species. The ammonium sulfates can be removed by appropriate heat treatment, while $MnSO_4$ cannot be recovered in the SCR. SCR activity of the MnO_x/PG catalyst was enhanced obviously after heat treatment for the poisoned catalysts, which indicated that the formation of $MnSO_4$ was not the key factor for the deactivation of catalysts. The adsorbed sulfur can enhance the surface acidity of catalysts significantly and thus improve the catalyst's activity. The main mechanism of the deactivation for MnO_x/PG catalysts was that SO_2 in the flue gas was oxidized continuously and formed ammonium sulfate with NH_3. The ammonium sulfates were difficult to decompose in low temperature, which resulted in the blocking of active sites.

Key words: MnO_x/PG catalysts ammonium sulfates $MnSO_4$ heat treatment

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